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СИНТЕЗ И ЭЛЕКТРОХИМИЧЕСКИЕ СВОЙСТВА Fe (III)-ЭТИОПОРФИРИНА II И ЕГО 5,15-БИС(ПИРИД-3-ИЛ)-ПРОИЗВОДНОГО

Н.М. Березина, Do Ngoc Minh, М.И. Базанов, А.С. Семейкин, А.А. Максимова

Надежда Михайловна Березина®, Михаил Иванович Базанов, Александра Александровна Максимова
Кафедра аналитической химии, Ивановский государственный химико-технологический университет,
просп. Шереметевский, 7, Иваново, Российская Федерация, 153000
E-mail: sky_berezina@rambler.ru®, bazanov@isuct.ru

Александр Станиславович Семейкин
Кафедра органической химии, Ивановский государственный химико-технологический университет,
просп. Шереметевский, 7, Иваново, Российская Федерация, 153000
E-mail: semeikin@isuct.ru

Do Ngoc Minh
Institute of Marine Economy and Engineering, Ba Ria - Vung Tau University, Truong Cong Dinh Str., 83,
Vungtau, 790000, Vietnam
E-mail: dongominh@mail.ru

В работе синтезированы и охарактеризованы 3,7,13,17-тетраметил-2,8,12,18-
тетраэтилпорфин железо (III) ацетат [(AcO)FeTMeTEtP] и 5,15-бис(пирид-3-ил)-3,7,13,
17-тетраметил-2,8,12,18-тетраэтилпорфин железо (III) ацетат [(OAc)OFe(Py-3)2TMeTEtP].
Методом циклической вольтамперометрии изучены электрохимические свойства и электрокатализитическая активность комплексов в реакции электровосстановления молекулярного кислорода в 0,1М растворе КОН. Проведен сравнительный анализ по влиянию комплексообразования, а также функционального замещения в молекуле (введение одного или двух пиридильных фрагментов в мезо-положения макроцикла) на электрохимические параметры и активность алкилзамеченного и пиридилзамеченного порфиринов в реакции ионизации молекулярного кислорода. Исследование электрохимического поведения комплексов близкого строения в рассматриваемых условиях показало существенное влияние пиридильного заместителя на изучаемые свойства. Полученные в нашей работе экспериментальные и литературные данные показали, что для (AcO)FeTMeTEtP и (AcO)Fe(Py-3)2TMeTEtP характерны редокс-процессы с участием как порfirинового макролигана (L ↔ L-, L- ↔ L2-), так и металла (Fe3+ ↔ Fe2+, Fe2+ ↔ Fe+). Обнаружено, что для (AcO)FeTMeTEtP, (Cl)Fe(Py-3)HMeDEtP и (AcO)Fe(Py-3)2TMeTEtP процесс электровосстановления центрального иона металла Fe3+ ↔ Fe2+ протекает при дополнительном введении в систему молекулярного кислорода. Результаты исследования электрокатализитической активности тетрапиррольных соединений в водно-щелочной среде позволяют сделать заключение о положительном влиянии как комплексообразования, так и введения электронодонорных алькильных заместителей в порфириный макроцикл на процесс электровосстановления молекулярного кислорода. Катализитическая активность изученных соединений в реакции ионизации кислорода возрастает согласно снижению потенциала электровосстановления O2 [E1/2(O2)] в ряду: H2TMeTEtP < (AcO)FeTMeTEtP < < (AcO)Fe(Py-3)2TMeTEtP.

Ключевые слова: порфиринов, Fe-комплексы, вольтамперометрия, электровосстановление, молекулярный кислород
SYNTHESIS AND ELECTROCHEMICAL CHARACTERISTICS OF Fe (III)-ETIO Porphyrin II AND ITS 5,15-BIS(PYRID-3-YL) DERIVATIVE

N.M. Berezina, Do Ngoc Minh, M.I. Bazanov, A.S. Semeikin, A.A. Maksimova

Department of Analytical Chemistry, Ivanovo State University of Chemistry and Technology, Sheremetevsky Ave., 7, Ivanovo, 153000, Russia
E-mail: sky_berezina@rambler.ru *, bazanov@isuct.ru

Department of Organic Chemistry, Ivanovo State University of Chemistry and Technology, Sheremetevsky Ave., 7, Ivanovo, 153000, Russia
E-mail: semeikin@isuct.ru

Institute of Marine Economy and Engineering, Ba Ria - Vung Tau University, Truong Cong Dinh st., 83, Vung-tau, 790000, Vietnam
E-mail: dongocminh@mail.ru

In this work acetato(3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphinato)iron (III) [(AcO)FeTMeTEtP] and acetato[5,15-bis(pyrid-3-yl)-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphinato]iron(III) [(OAc)OFe(Py-3)2TMeTEtP] have been synthesized and characterized. Electrochemical properties and electrocatalytic activity of complexes in oxygen electoreduction reaction in 0.1M KOH aqueous solution were studied by the cyclic voltammetry. The comparative analysis of the effect of complex formation, as well as functional substitution in the molecule (the introduction of one or two pyridyl fragments into meso-positions of the macrocycle) on the electrochemical parameters and activity of alkyl-substituted and pyridyl-substituted porphyrins in oxygen electoreduction reaction were carried out. The research of electrochemical behavior of complexes with close structure in experimental conditions has showed that a pyridyl substituent significantly affects the studied properties. The published data and obtained in our work have showed that (AcO)FeTMeTEtP and (AcO)Fe(Py-3)2TMeTEtP are characterized by redox processes involving both the porphyrin macrocycle (L ↔ L̄, L̄ ↔ L̄̄), and metal (Fe3+ ↔ Fe2+, Fe2+ ↔ Fe+). It should be noted that the process of electoreduction of the central metal ion (Fe3+ ↔ Fe2+) proceeds under additional introduction of oxygen into the system for the (AcO)FeTMeTEtP, (Cl)Fe(Py-3)HMeDEtP and (AcO)Fe(Py-3)2TMeTEtP. The results of investigation of the electrocatalytic activity of tetrapyrrole compounds in an aqueous-alkaline medium allows one to make a conclusion about the positive effect of complexation and the introduction of electron-donor substitutes in the porphyrin macrocycle on the electoreduction process of molecular oxygen. The electrocatalytic activity of the studied compounds in the oxygen ionization reaction were increased, according to the decrease in the half-wave potential of O2 [E1/2(O2)] in the series: H2TMeTEtP < (AcO)FeTMeTEtP < (AcO)Fe(Py-3)2TMeTEtP.

Key words: porphyrins, Fe-complexes, voltammetry, electoreduction, molecular oxygen

INTRODUCTION

Octaalkylporphyrin derivatives are the first synthetic porphyrins which have been investigated in detail by means of different electrochemical methods [1]. The electrochemical behavior of these compounds is that they are stepwise oxidized or reduced at the...
p-conjugated system to give $\pi$-cation radicals, dications and $\pi$-anion radicals, dianions. For metallooctae-thylporphyrins containing metal ions $\text{Zn}^{2+}$ and $\text{Mg}^{2+}$, the $\pi$-conjugated system undergoes electrochemical conversions, but in the case of $\text{Fe (III)}$, $\text{Co (II)}$, $\text{Mn (III)}$-complexes electrochemical processes both at the $\pi$-conjugated system and at the central metal ions are observed. The first comprehensive comparison of electrode reactions involving the formation of $\pi$-anion radicals and $\pi$-cation radicals was described in the work. According to this work, electrochemistry of twenty-five octaethylporphyrins with different metal ions has been investigated by cyclic voltammetry in BuCN (valeronitrile) for oxidation, and in DMSO (dimethylsulfoxide) for reduction. It was found that the potential difference $E_{1/2}$ between the first oxidation stage with the formation of the $\pi$-cation radical and the first reduction stage to obtain the $\pi$-anion radical is $2.25 \pm 0.15$ V. This value is close to the theoretically calculated value of the energy difference between HOMO and LUMO ($2.18$ V), from which the electron is removed or to which it is attached for most metalloporphyrins [2]. Additionally, the potential difference $E_{1/2}$ between the first and second reduction stages is $0.42 \pm 0.05$ V, and the potential difference $E_{1/2}$ between the first and second oxidation stages is $0.29 \pm 0.05$ V. These potential differences do not depend on the degree of oxidation of the central metal ion.

Electrochemical properties of porphyrin alkyl-derivatives: $2,8,12,18$-tetramethyl-3,7,13,17-tetraethylporphine ($\text{H}_2\text{TMeTEtP}$), octamethylporphine ($\text{H}_2\text{OMeP}$), $2,8,12,-18$-tetramethyl-3,7,13,17-tetrabuthylporphine ($\text{H}_2\text{TMeTBuP}$) and its Co complex in composition with technical elemental carbon (TEC) in a KOH aqueous solution have been described in [3]. The free ligands are characterized by two electroreduction processes of tetrapyrrol macrocycle to form $\pi$-anion radical and dianion. In the case of Co-complex an additional process of oxidation of the central metal ion Co(II) is observed. It was also found that by increasing length of alkyl substituents, the redox potentials of the observed processes are shifted to the anode region of potentials, i.e. a decrease in the induction effect on the macrocycle contributes to its reduction.

In the present work the results of studying electrochemical behavior and electrocatalytic activity of ($\text{OAc}$)$\text{Fe(III)}$-complexes (Fig. 1) in oxygen reduction reaction in aqueous alkaline solution were presented for the first time. The comparative characteristics of the effect of complex formation, as well as functional substitution in the molecule (the introduction of one or two pyridyl fragments into $\text{meso}$-positions of the macrocycle) on the electrochemical parameters and activity of alkyl-substituted and pyridyl-substituted porphyrins were carried out.

**EXPERIMENTAL**

Porphyrin-ligands were synthesized according to [4,5]. Metal complexes ($\text{AcO}$)FeTMeTEtP and ($\text{OAc}$)OFe (Py-3)$_2$TMeTEtP were synthesized according to the methods described below.
**Acetato(3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphinato)iron(III)** \((\text{AcO})\text{FeTMeTEtP}\). 500 mg of iron powder was added to a solution of 50 mg (0.081 mmol) of the ligand \(\text{H}_2\text{TMeTEtP}\) in 5 ml of \(\text{CH}_3\text{COOH}\). The reaction mixture was boiled for 2 h, cooled, and the powder was filtered off. 20 ml of water was added to the obtained solution that was neutralized with an ammonia solution. The precipitate was filtered off, dissolved in chloroform, chromatographed (Al\(_2\)O\(_3\), eluent: chloroform). Yield – 0.030g (50%). Mass-spectrometry was performed with a layer (0.2-0.3 mm) of an active mass, which was prepared in an ethyl alcohol, involved the carbon support (TEC – technical elemental carbon P-514 (GOST 7885-86) with the ash content 0.45%), the fluoroplastic suspension (6% FP-4D) and studied substance in weight ratio 7:2:1.

The measurements were carried out by using the potentiosstat-galvanostat «J-31P». Potentials of cathodic \((E_c)\) and anodic \((E_a)\) peaks for observed processes involving studied compounds were fixed with the accuracy of ±0.01 V. The values of redox potentials were determined as the average in a series of 5-6 parallel experiments. The obtained experimental results and calculated data are presented in Table and in Fig. 2, 3.

**RESULTS AND DISCUSSION**

**Electrochemical properties in an inert medium**

When an electrolyte is purged with argon, on the cyclic voltammetric curves for electrodes modified with \(\text{H}_2\text{TMeTEtP}\) and \((\text{AcO})\text{FeTMeTEtP}\) two general sequential processes of electroreduction of the macrocycle \([\text{process I (L}_2^2\leftrightarrow\text{L}}\text{O}_2^2\]\), \([\text{process II (L}_2^2\leftrightarrow\text{L}^2\text{O}_2^2]\), \(\text{Table}\), related to the attachment of electrons to the system of a macrocyclic ligand, are observed (Fig. 2).

For the metal complex \((\text{AcO})\text{FeTMeTEtP}\), additional processes \((\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}\) and \(\text{Fe}^{2+} \leftrightarrow \text{Fe}^+\) localized on the metal atom, were found (Fig. 2).

**Table**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(E_{1/2}(\text{V}))</th>
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<tbody>
<tr>
<td>(\text{H}_2\text{TMeTEtP (Eti0 II) [3]})</td>
<td>-</td>
<td>-0.74</td>
</tr>
<tr>
<td>((\text{AcO})\text{FeTMeTEtP})</td>
<td>-0.49</td>
<td>-0.61</td>
</tr>
<tr>
<td>((\text{Cl})\text{OFe(Py-3)}\text{HMeDEtP [7]})</td>
<td>-0.29*</td>
<td>-0.53</td>
</tr>
<tr>
<td>((\text{OAc})\text{OFe(Py-3)}\text{TMeTEtP [8]})</td>
<td>-0.38*</td>
<td>-0.62</td>
</tr>
<tr>
<td>((\text{OAc})\text{OFe(Py-4)}\text{TMeTEtP [8]})</td>
<td>-0.69</td>
<td>-0.87</td>
</tr>
<tr>
<td>(\text{TEC})</td>
<td>-</td>
<td>-1.04**</td>
</tr>
</tbody>
</table>

**Notes:** * – values of potential at oxygen introducing into the system, ** – \(\text{L}^2\leftrightarrow\text{L}^2\), \(E_{1/2} = (E_c + E_a)/2\)

**Electrochemical parameters of redox processes (vs Ag/AgCl) and the process of oxygen electroreduction in 0.1M KOH solution, \(v = 20 \text{ mV s}^{-1}\)**

**Таблица. Электрохимические параметры редокс-процессов (vs Ag/AgCl) и процесса электроокисления кислорода в 0.1M растворе KOH. \(v = 20 \text{ mB s}^{-1}\)**

<table>
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<td>-1.04**</td>
</tr>
</tbody>
</table>

The first stage of electroreduction \((\text{AcO})\text{FeTMeTEtP}\) under the considered conditions proceeds at more positive potentials, in comparison with the ligand. The redox potential \(E_{1/2}^{\text{II}}\) of the second reduction process \((\text{L}^- \leftrightarrow \text{L}^2^-)\) is shifted by 80 mV into the positive region, that indicates an increase in the reducing ability of transition metals complexes (in this case, iron).

According to the obtained and previously published data (Table), the introduction of one electroactive substituent into the meso-position of the porphin leads to the fact that it possible to \((\text{Cl})\text{OFe(Py-3)}\text{HMeDEtP}\) is reduced in the second stage, compared with \((\text{AcO})\text{FeTMeTEtP}\).

The electrochemical behavior of the bipyridyl complex \((\text{AcO})\text{Fe(Py-3)}\text{TMeTEtP}\) and the mono-pyridyl analog \((\text{Cl})\text{Fe(Py-3)}\text{HMeDEtP}\) is practically identical in the number of stages of the electrochemical processes, with some weakness of the reducing properties for the bis-pyridyl complex (Fig. 2, Table), in contrast to the complex \((\text{AcO})\text{Fe(Py-4)}\text{TMeTEtP}\).
For the complex (AcO)Fe(Py-3)₂TMeTEtP, the following features can be noted:

- The process of electroreduction (electrooxidation) Fe³⁺ ↔ Fe²⁺ is fixed only in the case of additional introduction of molecular oxygen into the electrolyte. The observed value E₁/₂ = -0.38 V and the reversibility parameter of this process ΔE = 0.21 V indicate a less expressed ability to reduce the central metal ion with additional introduction of the second pyridyl fragment into the molecule of the porphyrin ligand. The same conclusion can be drawn for the second stage of electroreduction of the central metal ion (Fe²⁺ ↔ Fe⁺), where for Fe (III) complex containing the bispyridyl, the value E₁/₂ = -0.81 V is shifted to region of negative values by 100 mV, compared with the mono-pyridyl analog [for the complex (Cl)Fe(Py-3)HMe-DEtP it is -0.71 V]. It should be noted that these changes could be affected not only by the amount of pyridyl fragments in the molecule of the porphyrin compound, but also by the nature of the extra ligand (for complex (Cl)Fe(Py-3)HMeDEtP - chloride ion, for (AcO)Fe(Py-3)₂TMeTEtP – acetate ion).

- The first stage of electroreduction (electrooxidation) of the porphyrin macrocycle is also characterized by a shift of the redox potential (E₁/₂ = -0.62 V) to the negative range by 90 mV, compared with (Cl)Fe(Py-3)HMeDEtP (E₁/₂ = -0.53 V). The second stage of electroreduction is also characterized by a displacement of the peak potential in the region of negative values by 80 mV.

It should be noted that for the (AcO)FeTMeTEtP, (Cl)Fe(Py-3)HMeDEtP, (AcO)Fe(Py-3)₂TMeTEtP, the process of electroreduction of the central metal ion (Fe³⁺ ↔ Fe²⁺) proceeds under additional introduction of oxygen into the system.

Electrocatalytic properties in ionization reaction of molecular oxygen

In order to conduct an analysis of the electrocatalytic activity (AcO)FeTMeTEtP in the electroreduction reaction of molecular oxygen, I,E-curves (Fig. 2, 3, curve 2), corresponding to the saturation of the electrolyte with oxygen, were obtained. The increase in the catalytic activity of the investigated compounds leads to the depolarization effect, which is demonstrated in the displacement of the electroreduction wave of molecular oxygen and the half-wave potential \[E₁/₂(O₂)\] into the region of positive values in comparison with the system without a catalyst. Comparing the values of \[E₁/₂(O₂)\] (Table), we can conclude that the catalytic activity of the studied compounds in the electroreduction reaction of molecular oxygen increases in the series: \(H₂TMeTEtP < (AcO)FeTMeTEtP < (AcO)Fe(Py-3)₂TMeTEtP\).

The conducted investigation of the electrocatalytic activity of tetrapyrrole compounds in an aqueous-alkaline medium allows one to make a conclusion about the positive effect of complexation and the introduction of electron-donor substitutes in the porphyrin macrocycle on the electroreduction process of molecular oxygen. It should be noted that the additional introduction of pyridyl substituents into the macrocycle leads to an increase in the electrocatalytic effect in comparison with the macroheterocycle (AcO)FeTMeTEtP.

CONCLUSION

The comparative analysis of the obtained in our work and published data (Table) showed that (AcO)FeTMeTEtP and (AcO)Fe(Py-3)₂TMeTEtP are
characterized by redox processes involving both the porphyrin macrocycle ($L \leftrightarrow L^-$, $L^- \leftrightarrow L^{2-}$), and metal ($Fe^{2+} \leftrightarrow Fe^{3+}$, $Fe^{3+} \leftrightarrow Fe^{4+}$). It has been established that complexation leads to the fact that the process of electroreduction of the tetrapyrrole macrocycle proceeds more easily, and the electrocatalytic activity of the compounds in the electroreduction reaction of molecular oxygen significantly increases.

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